

The very long range nature of capillary interactions in liquid films

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Micron-sized objects confined in thin liquid films interact through forces mediated by the deformed liquid-air interface. This capillary interactions provide a powerful driving mechanism for the self-assembly of ordered structures such as photonic materials or protein crystals. Direct probing of capillary interactions requires a controlled force field to independently manipulate small objects while avoiding any physical contact with the interface. We demonstrate how optical micro-manipulation allows the direct measurement of capillary interactions between two micron sized spheres in a free standing liquid film. The force falls off as an inverse power law in particles separation. We derive and validate an explicit expression for this exponent whose magnitude is mainly governed by particles size. For micron-sized objects we found an exponent close to, but smaller than one, making capillary interactions a unique example of strong and very long ranged forces in the mesoscopic world.

It is a well known fact that small objects floating on a liquid surface cluster together. Bubbles on the surface of a soap solution[1] or cereals in a bowl of milk[2] attract each other with long range forces arising from the interface deformation under particles weight (or buoyancy for bubbles). Close packed configurations for such macroscopic objects are found to minimize gravitational potential energy. Shrinking lengths to the mesoscopic scale, particles weight soon become too weak to produce any significant deformation and hence attraction. However if the particles are confined in thin liquid films a deformation of the interface is unavoidable. This is the case, for example, of a colloidal suspension drying on a solid substrate, or dispersed in a free standing thin film. When the thickness of the liquid film becomes smaller than the bead diameter, the interface has to deform with an increase in surface energy. The liquid interface will then react on the particles with forces aiming to reach a minimum surface (energy) configuration, that usually corresponds to close packed two dimensional crystals[3]. Such phenomena, already observed by Perrin in 1909[4], have attracted considerable interest in recent times due to their relevance for the engineering of photonic materials[5] and protein crystallography[6]. Consequently, a strong effort has been devoted to the theoretical analysis of the involved forces, resulting in a long series of papers reviewed in[7]. Prediction for macroscopic objects have been confirmed by experiments on immersed cylinders [8] or particles attached to holders[9].

However no experiment so far has been able to directly measure the strong capillary force acting between an isolated pair of mesoscopic objects, despite the fact that it is in the mesoscopic and nanoscopic realm that this effect finds the most interesting applications. Any physical contact with the particles would inevitably produce a significant deformation of the liquid-air interface and dramatically affect the interaction. On the other hand, due to long ranged hydrodynamic interactions in 2D, particles mobility are very sensitive to interparticle distances

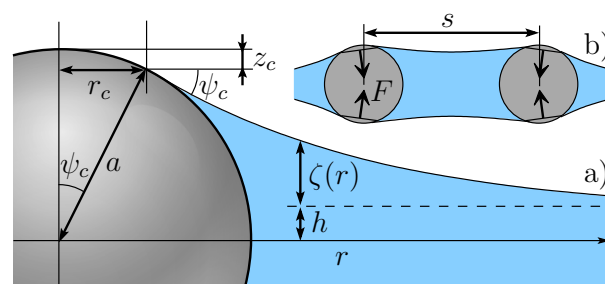


FIG. 1: (Color online) Wetting geometry. Complete wetting is assumed, so that the liquid film wraps the particle inside a spherical cap of radius r_c . For $r > r_c$ the liquid-air interface is free-standing and slowly falls to the large distance height h . The local height of the interface measured from h is indicated by the function $\zeta(r)$, whose gradients are assumed to be small everywhere ($\psi_c \ll 1$).

and force measurements are difficult to deduce from particles trajectories. A static, highly non-invasive method is required for a direct and reliable measurement of these interactions.

In this Letter we demonstrate how optical micro-manipulation [10] allows the precise measurement of capillary interactions between two micron sized spheres confined in a free standing thin liquid film. Holographic optical tweezers [11] allow to isolate a single pair of particles and scan their relative distance from close contact to several tens of diameters. Capillary forces will tend to push the particles towards each other and out of the optical traps until the restoring trap forces will balance the attractive force. The intensity of capillary force can be then deduced by measuring particles displacements from trap centers, after trap calibration. Working in a free standing liquid film is essential for accurate capillary force determinations since no particle-substrate interactions have to be taken into account.

The force law can be anticipated by calculating the surface tension forces acting on a pair of spherical objects

confined in a thin liquid film. Kralchewsky et al.[12] derived the shape of the meniscus around the two particles using the method of matched asymptotic expansions. An implicit expression for the force law was obtained, whose evaluation required the numerical solution of a system of nonlinear equations in the accessible system parameters. Confining here to mesoscopic objects, we show that Kralchewsky solution for the force can be very well approximated by an inverse power law whose parameters have an explicit expression in terms of the system's physical properties. We assume complete wetting (zero contact angle) with the liquid surface departing from a contact ring of radius r_c with continuous slope angle ψ_c (Fig. 1a). Surface tension will exert a force on the contact ring whose resultant is orthogonal to the ring plane and has a modulus:

$$F = \gamma 2\pi r_c \sin \psi_c \quad (1)$$

where γ is the liquid-air surface tension ($\gamma \simeq 35$ mN/m in our experiment). For small gradients $r_c = a \sin \psi_c \sim a\psi_c$, $z_c = a(1 - \cos \psi_c) \simeq a\psi_c^2/2$, and the force $F \simeq 4\pi\gamma z_c$ is then proportional to z_c with a strength of order 1 nN/nm. The order of magnitude of other forces into play is 1 pN for particle's weight and 100 pN for the maximum optical force exerted by our trap. The interface is supposed to be flat and horizontal far from the particle and we indicate with $\zeta(r)$ the local vertical displacement of the interface from this reference surface. In the small gradient approximation, Laplace equation for the pressure drop across free standing portion of the upper surface ($r > r_c$) reads[13]:

$$\gamma \nabla^2 \zeta(r) = \rho g \zeta(r) \quad (2)$$

where ρ is the liquid density and g the acceleration due to gravity. The only axisymmetrical solution to (2) vanishing at infinity takes the form[14]:

$$\zeta(r) = -\frac{\tan \psi_c}{q} \frac{K_0(qr)}{K_1(qr_c)} \quad (3)$$

where $K_i(x)$ is the modified Bessel function of i th order[15] and $q^{-1} = \sqrt{\gamma/\rho g}$ is the capillary length. This is the length scale below which gravitational forces play no role in determining the interface shape and it's about 2 mm in typical solvents. Therefore we can safely replace $K_0(x)$ and $K_1(x)$ with their small argument expansion and write for small gradients:

$$\zeta(r) = -2z_c [\log(qr/2) + \gamma_e] \quad (4)$$

where γ_e is the Euler-Mascheroni constant. At the micron scale gravitational energy will be negligible and the

bottom surface will have a symmetrical shape to the top one. Therefore two equally strong capillary forces will act on the top and bottom contact rings of an isolated particles but they will cancel out giving no net force. When a second particle is introduced in the film at a distance s , it will in turn contribute to the interfaces deformation producing a tilt of the contact lines around the first particle (Fig. 1b). For small deformations we can still think of contact lines as circles but this time slightly tilted. Within the superposition approximation by Nicolson[14], the amount of tilt would simply be given by the gradient of the surface deformation produced by an isolated particle at the location of the second one. According to (4) the interface height around an isolated particle is expected to decay logarithmically with the distance producing a tilt of the contact lines that falls off as the inverse interparticle distance. Capillary forces F acting on the contact rings will not be balanced anymore but a net attractive force would appear whose intensity is given by the projections of F on the film reference plane:

$$f(s) = 2F(s) \left. \frac{\partial \zeta(r)}{\partial r} \right|_{r=s} = 16\pi\gamma z_c^2(s) \frac{1}{s} \quad (5)$$

where s is the interparticle distance. The resulting force is then proportional to the square of z_c and inversely proportional to the distance separating the particles. In analogy with Coulomb electrostatic force in 2D, the quantity z_c is usually called the ‘‘capillary charge’’ of the particle[16]. However, the capillary charge is not an intrinsic constant property but a slowly varying function of particle separation. This function can be calculated by imposing the continuity and differentiability of the interface across the contact ring.

$$\zeta(r_c) + \zeta(s) + h = a - z_c \quad (6)$$

$$r_c = a \sin \psi_c \sim \sqrt{2az_c} \quad (7)$$

where we rely on the superposition approximation [14] to express the interface vertical displacement field as the sum of two single particle displacement fields (4). We are also assuming in (6) that the deformation field $\zeta(s)$ produced by one particle is constant over the contact line of the other. Equations 6,7 can be solved analytically giving:

$$z_c(s) = \frac{a - h}{-W[-q^4 s^2 a(a - h) \exp[4\gamma_e - 1]/8]} \quad (8)$$

Where W is the Lambert-W function [17]. The above expression for z_c is a slowly varying function of s in mesoscopic systems ($a < s \ll q^{-1}$) and it can be well approximated by its logarithmic expansion about $s = 2a$:

$$z_c(s) \sim z_0(s/2a)^\alpha \quad (9)$$

$$z_0 = z_c(2a) \quad (10)$$

$$\alpha = \left. \frac{d \log z_c}{d \log s} \right|_{s=2a} = \frac{2z_0}{a - h - z_0} \quad (11)$$

Accounting for changes in z_c the attractive force (5) will still display a power law behavior but with an exponent smaller than one:

$$f(s) = \frac{16\pi\gamma z_0^2}{2a} \left(\frac{2a}{s} \right)^{1-2\alpha} \quad (12)$$

where α is an explicit function of the three lengths: particle size, film thickness, capillary length of the solvent. The exponent $1 - 2\alpha$ is equal to 1 for $h \rightarrow a$ but then quickly drops to a fairly constant value as soon as h is small enough to produce significative forces (~ 1 pN $\sim 10^3 K_B T/a$). This constant value depends practically only on the particle size and varies very little when using different typical solvent properties. Changing particle size from 10 nm to 10 μ m produces a corresponding exponent variation in the range 0.92 to 0.82. For our particle size we predict an exponent of 0.86.

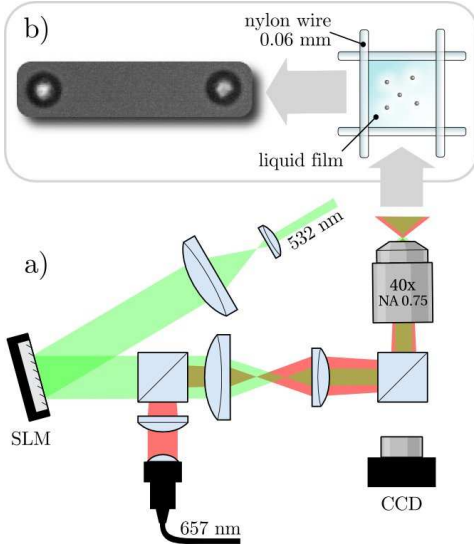


FIG. 2: (Color online) Schematic view of the experimental setup described in text.

A schematic view of the experimental setup is reported in Fig. 2a.

Latex beads (5.7 μ m diameter) are dispersed in a 2/3 water - 1/3 glycerol mixture with added 0.2% wt surfactant (SDS). A thin film is obtained by sweeping the solution on a square frame (10 mm side) of nylon wires (60 μ m thickness). The free standing liquid film is enclosed

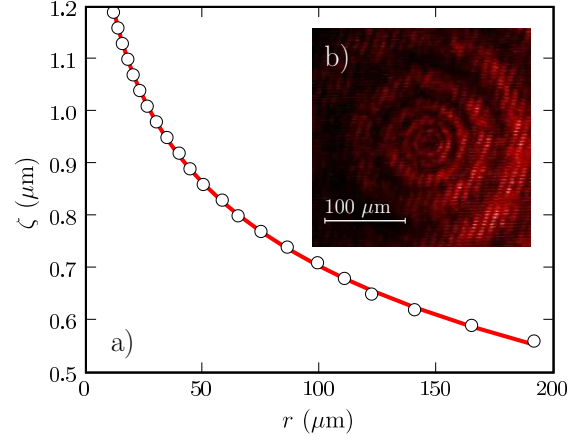


FIG. 3: (Color online) Film thickness profile around an isolated particle. b) Monochromatic light reflected off the film displays interference fringes centered around an isolated trapped particle. A period in the fringe pattern corresponds to 240 nm thickness variation. Figure a) reports as open circles the extracted film height $\zeta(r)$ versus distance from particle center r together with a logarithmic fit (red line).

in a humidity chamber and placed over the 40x objective of an inverted optical microscope (Nikon TE2000-U). The same objective is used to focus the laser beam ($\lambda=532$ nm) reflected off a spatial light modulator (Holoeye LCR-2500) into two, dynamically reconfigurable, optical traps [11]. Axial confinement is guaranteed by the normal components of capillary forces. We can also access the thickness variations around an isolated particle by viewing the film under reflected monochromatic light. To this end a red diode laser beam, overlapped to the trapping green beam, is focused by the same microscope objective far from the film surface. The observed portion of the red beam wavefront is approximately plane and the film reflectance then varies with $\cos[4\pi\zeta(r)n/\lambda]$ giving interference rings. $n = 1.37$ is the refractive index of the liquid mixture and $\lambda = 657$ nm the red laser wavelength. The distorted film will then show ring shaped interference fringes centered on the trapped particle (Fig. 3b). The thickness profile around an isolated trapped particle can be extracted (within an additive constant) and is reported here in Fig. 3a as open circles. A clean logarithmic shape is found up to 200 μ m, in perfect agreement to prediction in (4), as shown by the logarithmic fit curve (red line).

To extract the force law one of the two traps is held fixed while the other is continuously scanned through different distances with a step of 2 μ m. An image of the two particle is digitally recorded (Fig. 2b) for every scan step and subsequently used to extract particle positions. Due to liquid drainage, the film is slowly but constantly thinning. When the thickness is so small that optical forces cannot balance the capillary interaction,

one of the two particles jumps out of the trap and collapses onto the other. Until that time we can extract the attractive capillary force from the interparticle distance. Calling k_1 and k_2 the two trap elastic strengths, each particle will be displaced towards the other by a distance $\Delta x_i = f/k_i$. The observed interparticle separation will be then smaller than trap separation by an amount: $\Delta s = (\Delta x_1 + \Delta x_2) = f(1/k_1 + 1/k_2) = f/k'$. Particle distance will actually fluctuate due to Brownian motion with a mean squared value given by [18]: $\langle \Delta d^2 \rangle = K_B T / k'$ which can be used to experimentally determine $k' = 29$ pN/ μm .

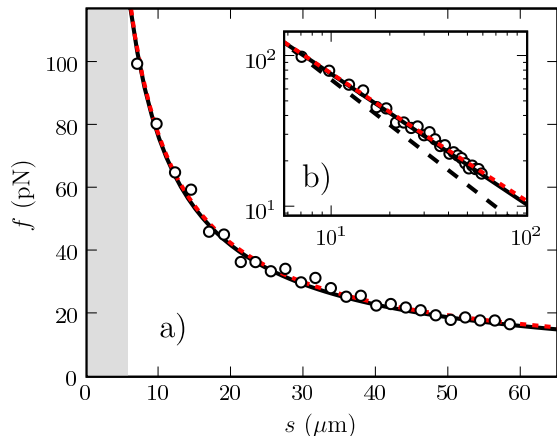


FIG. 4: (Color online) Intensity of the capillary interaction between two beads confined in a thin film, as a function of their relative distance. Open circles are experimental determinations. The black solid line represents a fit to the predicted power law (12) having the film thickness h as the only free parameter. Red dashed line is the full Kralchewsky theory[12] for the same h parameter. The gray region marks the unaccessible range of separations s smaller than close contact distance $2a$. Double log plot insert more immediately shows that the data are well represented by a power law. A $1/r$ law is also reported there, for reference, as a black dashed line.

As already discussed, the logarithmic film shape in Fig. 3 would lead, in the Nicolson approximation, to an attractive force decaying roughly as the inverse of interparticle distance. More precisely we would expect to find the power law in (12). Indeed a clean power law is found experimentally as evidenced by the double log plot reported in Fig. 4b. The overall behavior is very well fitted by the power law in (12) leaving the film thickness at large distance h as the only free parameter. We find $h = 2.2\mu\text{m} = 0.8a$ that makes an average gradient $\psi_c = 0.12$ confirming that the small gradient approximation is justified for our system. For this fitted h value we get a power law exponent $1 - 2\alpha = 0.86$. The full Kralchewsky prediction for the same parameter values, also reported in Fig. 4b, is almost completely overlapped to our power law expansion, confirming the goodness of our approximations.

We have shown how optical micromanipulation provides an unprecedented tool for investigating capillary forces which govern aggregation and self-assembly of colloids in liquid films. We provide a static force measurement of the capillary attraction between an isolated colloidal pair and perform a direct test of the theoretically predicted power law. The exponent of the power law is found to be close to, but smaller than one, making capillary forces a quite unique example of very long ranged interactions in the mesoscopic world. The experiment opens the way to a variety of further developments addressing the role of many body-effects, membrane elasticity, wetting properties, surfactant dynamics, hydrodynamic interactions in 2D. A deep insight into the nature of interface-mediated forces at the mesoscopic scale could suggest new routes to self-assembly of meso- and nano-structures[19]. Optical trapping of colloidal particles bound to lipid membranes [20] could also provide new insights in the dynamics of biomembrane inclusions[21].

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